IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATIONS : K.KATO, et al.
SERIAL NO. : 10/615,297
FILED : July 9, 2003.
FOR : PROCESS FOR PRODUCTION OF POLYALKYL-SUBSTITUTED AROMATIC ALDEHYDE
ART UNIT : 1621
EXAMINER : Johann Richter

DECLARATION UNDER 37 CFR 1.132

Honorable Commissioner of Patents and Trademarks
Washington, D.C. 20231

Sir:

I, KINJI KATO of 3-10, Mizushumakaigandori, Kurasiki-shi, Okayama, Japan, declare that;

1. I graduated from Department of Chemistry, Faculty of Science, Tohoku University (Doctor course) in March 1992 and entered Mitsubishi Gas Chemical Company, Inc. in April 1992. I have been in charge of research and development of aromatic compound products in Mizushima Factory from January 1994, and have held the position up to the present time.

2. I am one of the named inventors of the present U. S. Patent Application as identified above, and familiar with the subject matter disclosed in the Application.

3. Experiment

Object of Experiment

The following experiments were carried out, in order to compare the performance of the formylation using HF-BF_3 catalyst of a polyalkyl-substituted aromatic compound having three to five C_1-C_3 alkyl groups and that of a polyalkyl-substituted aromatic compound having one or two alkyl group(s).

Procedures of Experiment

Using o-xylene as aromatic compound having two alkyl groups and ethyl benzene as aromatic compound having one alkyl group, following experiments were carried out.

Experiment A-1

A 500-ml autoclave equipped with a stirrer, three upper inlet nozzles, one bottom outlet nozzle and a jacket for controlling the inner temperature was used as a formylation reactor.

Into the autoclave cooled to -15℃ or lower by flowing a cooling medium through the jacket, were charged 50 g (2.5 mol) of hydrogen fluoride and 106 g (1.0 mol) of o-xylene. While controlling the temperature of the reaction solution -15℃ or lower, 102 g (1.5 mol) of boron trifluoride was added under stirring.

After the addition of boron trifluoride, the inner pressure of the autoclave was increased to 2 MPa by introducing carbon monoxide. During increasing the inner pressure of the autoclave, the liquid temperature was increased (maximum 5℃). After stirring for 20 minutes while maintaining the pressure at 2 MPa, the whole reaction mixture was drawn from the reactor into ice water. The liquid mixture was added with heptane and mixed thoroughly by shaking, followed by separation of the oil layer, which was then washed with water and analyzed by gas chromatography. As shown in Table A, the conversion of o-xylene was 64.8 mol% and selectivity of 3,4-dimethyl benzaldehyde was 94.4 mol%.

Experiment A-2

The same procedure as in Experiment A-1 was repeated except for changing the charge amount of hydrogen fluoride to 70 g (3.5 mol). The gas chromatographic analysis of the oil layer showed, as shown in Table A, the conversion of o-xylene was 89.5 mol% and selectivity of 3,4-dimethyl benzaldehyde was 97.5 mol%.

Experiment A-3

The same procedure as in Experiment A-1 was repeated except for changing the charge amount of hydrogen fluoride to 100 g (5.0 mol). The gas chromatographic analysis of the oil layer showed, as shown in Table A, the conversion of o-xylene was 97.5 mol% and selectivity of 3,4-dimethyl benzaldehyde was 97.3 mol%.

Experiment A-4

The same procedure as in Experiment A-1 was repeated except for changing the charge amount of hydrogen fluoride to 150 g (7.5 mol). The gas chromatographic analysis of the oil layer showed, as shown in Table A, the conversion of o-xylene was 100.0 mol% and

selectivity of 3,4-dimethyl benzaldehyde was 98.1 mol%.

Table A

	A-1	A-2	A-3	A-4
HF / o-xylene (molar ratio)	2.5	3.5	5.0	7.5
BF_3 / o-xylene (molar ratio)	1.5	1.5	1.5	1.5
Conversion (mol%)	64.8	89.5	97.5	100.0
Selectivity (mol%)	94.4	97.5	97.3	98.1
Yield (mol%)	61.2	87.2	94.9	98.1
Precipitation of solids	none	none	none	none

Experiment B-1

A 500-ml autoclave equipped with a stirrer, three upper inlet nozzles, one bottom outlet nozzle and a jacket for controlling the inner temperature was used as a formation reactor.

Into the autoclave cooled to -20℃ or lower by flowing a cooling medium through the jacket, were charged 50 g (2.5 mol) of hydrogen fluoride and 107 g (1.0 mol) of ethyl benzene. While controlling the temperature of the reaction solution -20℃ or lower, 102 g (1.5 mol) of boron trifluoride was added under stirring.

After the addition of boron trifluoride, the inner pressure of the autoclave was increased to 2 MPa by introducing carbon monoxide. During increasing the inner pressure of the autoclave, the liquid temperature was increased (maximum -5℃). After stirring for 20 minutes while maintaining the pressure at 2 MPa, the whole reaction mixture was drawn from the reactor into ice water. The liquid mixture was added with heptane and mixed thoroughly by shaking, followed by separation of the oil layer, which was then washed with water and analyzed by gas chromatography. As shown in Table B, the conversion of ethyl benzene was 93.3 mol% and selectivity of p-ethylbenzaldehyde was 9.7 mol%.

Experiment B-2

The same procedure as in Experiment B-1 was repeated except for changing the charge amount of hydrogen fluoride to 100 g (5.0 mol). The gas chromatographic analysis of the oil layer showed, as shown in Table B, the conversion of ethyl benzene was 99.6 mol% and selectivity of p-ethylbenzaldehyde was 14.5 mol%.

Experiment B-3

The same procedure as in Experiment B-1 was repeated except for changing the charge amount of hydrogen fluoride to 150 g (7.5 mol). The gas chromatographic analysis of

the oil layer showed, as shown in Table B, the conversion of ethyl benzene was 100.0 mol% and selectivity of p-ethylbenzaldehyde was 18.0 mol%.

Experiment B-4

The same procedure as in Experiment B-1 was repeated except for changing the charge amount of hydrogen fluoride to 200 g (10.0 mol). The gas chromatographic analysis of the oil layer showed, as shown in Table B, the conversion of ethyl benzene was 99.9 mol% and selectivity of p-ethylbenzaldehyde was 12.5 mol%.

Table B

	B-1	B-2	B-3	B-4
HF / ethyl benzene (molar ratio)	2.5	5.0	7.5	10.0
BF_3 / ethyl benzene (molar ratio)	1.5	1.5	1.5	1.5
Conversion (mol%)	93.3	99.6	100.0	99.9
Selectivity (mol%)	9.7	14.5	18.0	12.5
Yield (mol%)	9.1	14.4	18.0	12.5
Precipitation of solids	None	none	none	none

Results of the Experiment;

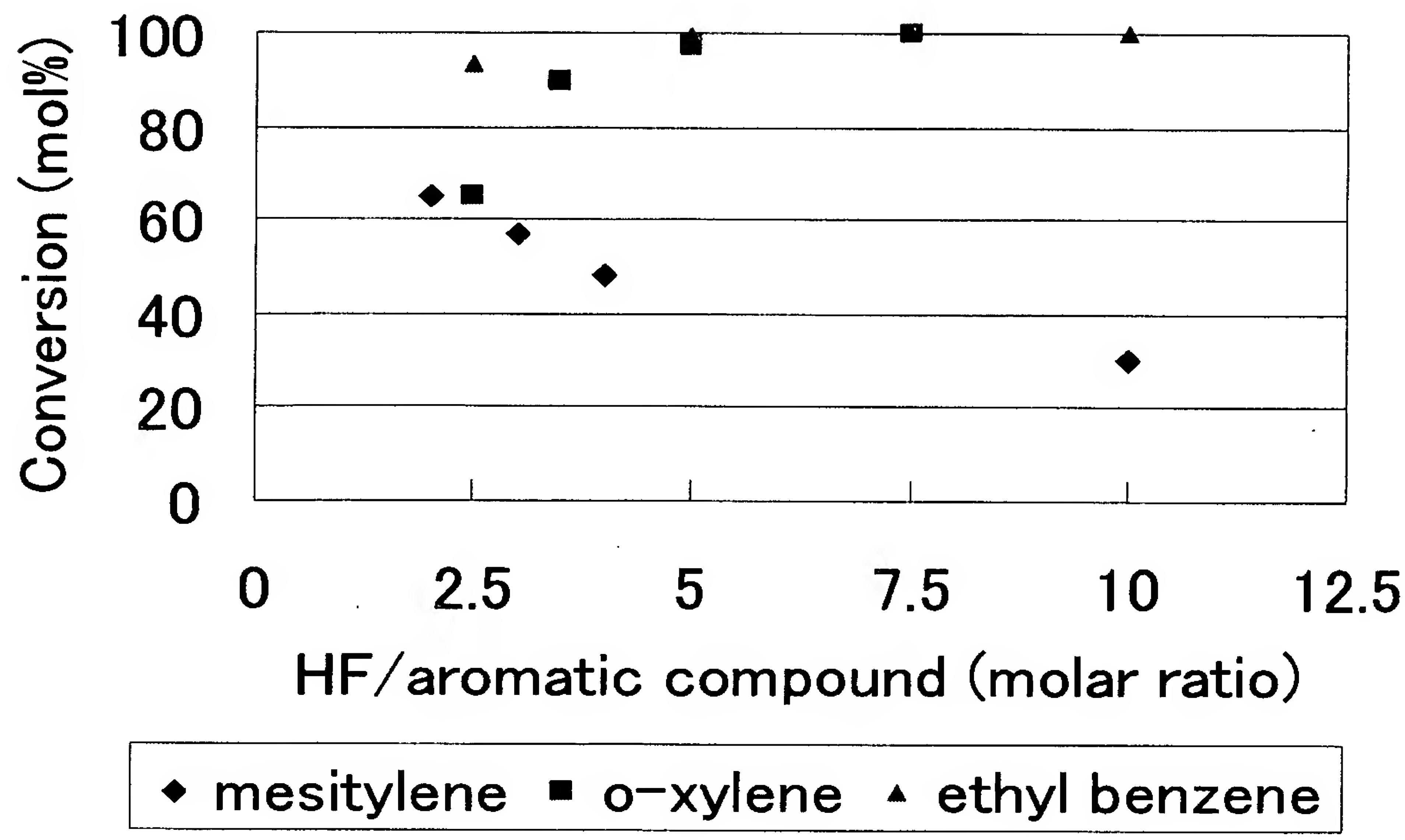
From Examples of the present invention and above Experiments, the conversion and yield of alkyl-substituted aromatic compound (mesitylene, o-xylene and ethyl benzene) at each hydrogen fluoride / alkyl-substituted aromatic compound ratio are shown as following.

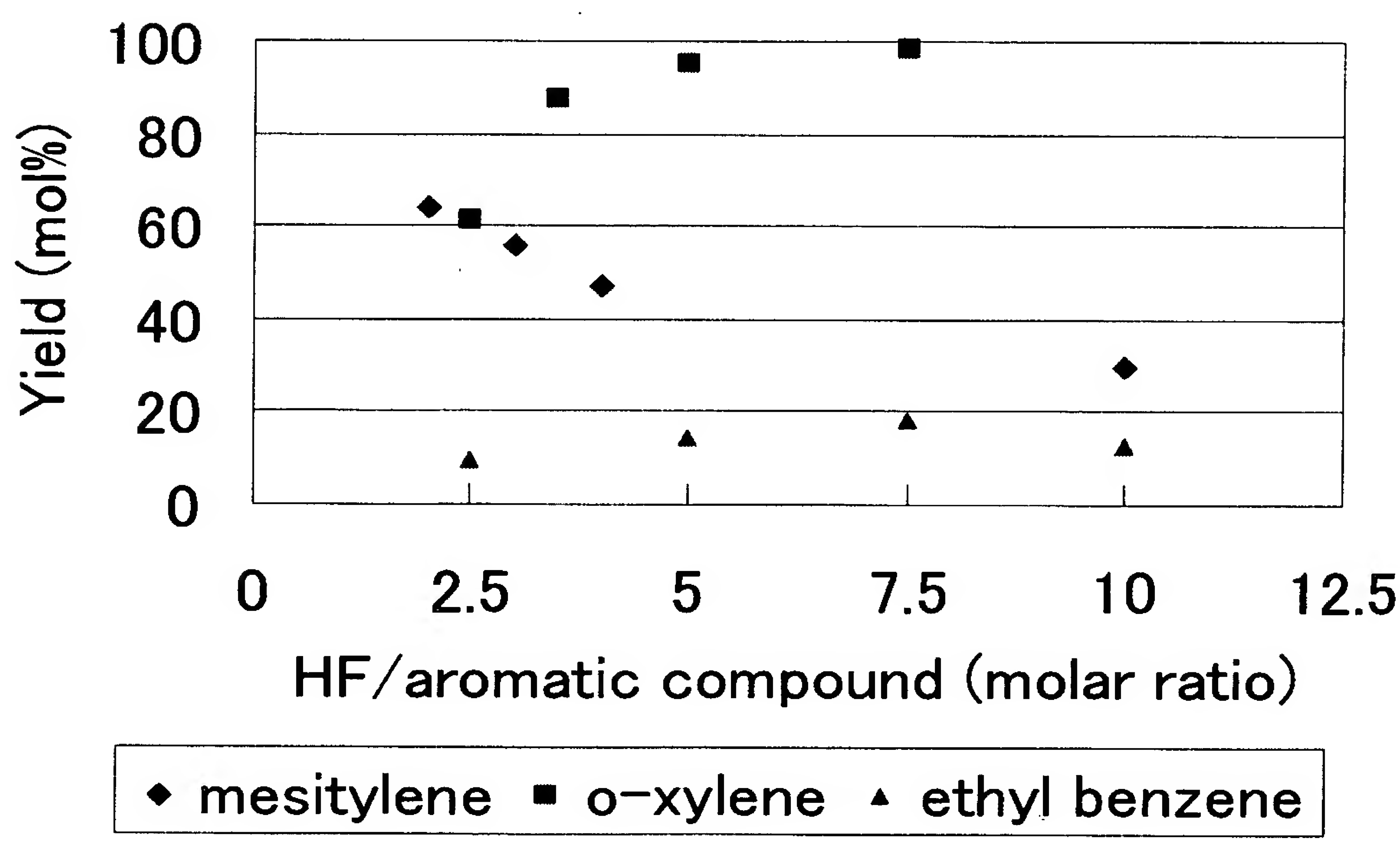
conversion

HF/ Arom. Comp. ratio	2.0	2.5	3.0	3.5	4.0	5.0	7.5	10.0
mesitylene	65		57		48			30
o-xylene		64.8		89.5		97.5	100	
ethyl benzene		93.3				99.6	100	99.9

yield

HF/ Arom. Comp. ratio	2.0	2.5	3.0	3.5	4.0	5.0	7.5	10.0
mesitylene	63.7		55.9		47.0			29.4
o-xylene		61.2		87.2		94.9	98.1	
ethyl benzene		9.1				14.4	18.0	12.5


Conversion (mol%)
100
80
60
40
20
0
0
2.5
5
7.5
10
12.5
HF/aromatic compound (molar ratio)
◆ mesitylene ■ o−xylene ▲ ethyl benzene


Yield (mol%)
100
80
60
40
20
0
0
2.5
5
7.5
10
12.5
HF/aromatic compound (molar ratio)
◆ mesitylene ■ o−xylene ▲ ethyl benzene

Consideration;

From above graph, the conversion of o-xylene and ethyl benzene, which were selected from alkyl-substituted aromatic compound having one or two alkyl group(s), increased according to HF increased, however, the conversion of mesitylene, which was selected from polyalkyl-alkyl-substituted aromatic compound having three to five alkyl groups, decreased according to HF increased. The yield of o-xylene increased according to HF increased, however, the yield of mesitylene decreased according to HF increased. The yield of ethyl benzene was very low because of low selectivity.

Then the amount of hydrogen fluoride was limited to 2.5 to 4.5 mol based on one mole of polyalkyl-substituted aromatic compound in the present invention because high yield was obtained and there were no precipitation of solids in this range. These differences of the performance at a formylation of a polyalkyl-substituted aromatic compound having three to five alkyl groups were not suggested from Fujiyama et al. The polyalkyl-substituted aromatic aldehyde is produced from polyalkyl-substituted aromatic compound having three to five alkyl groups efficiently with high selectivity and comparatively high yield by the present invention.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and beliefs are to be true; and further that these statement were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Kinji Kato

Kinji Kato

Date : August 27, 2004